COAL LIQUEFACTION BY STEAM PYROLYSIS

Robert A. Graff and Susan D. Brandes

The Clean Fuels Institute, The City College CUNY
New York, NY 10031

Introduction

A key to obtaining high liquid yields in steam pyrolysis of coal has been found to be pretreatment in steam at low temperature. In tests reported here, coal is pyrolyzed in steam at a pressure of 50 atm. by flash heating to temperatures from 870 to 980°C. In the absence of pretreatment about 23% of the coal's carbon is converted to liquid product. If, however, the coal is first exposed to 50 atm. of steam for less than 30 min. at temperatures from 320 to 360°C, over 50% carbon conversion to liquids is obtained in subsequent pyrolysis.

Experimental Methods

These experiments were conducted in a bench-scale batch reactor (Fig.1). In order to obtain rapid heating of coal, the sample is held in an external injection tube while the reactor is brought to temperature under a flow of superheated steam. The reactor is constructed of 2.5 cm i.d., 3.8 cm o.d. 304 stainless steel pipe and is 25 cm. in length. A trap of -8 + 10 mesh quartz chips, 2.5 cm deep, supported by a drilled steel plate is located at the center of the reactor. Heating is provided by an external furnace and electrical windings. Reaction temperature is read from a thermocouple in a well inserted from the bottom of the reactor and in contact with the trap.

Coal, held in the injection tube (5.1mm i.d.) by two quartz wool plugs, is injected into the reactor by a pulse of helium obtained from a 32.5 cc pulse tank charged to 82 atm. by opening a solenoid valve for a nominal 0.1 sec. Upon injection into the incoming stream of superheated steam, the sample is carried downward and deposited on the trap. It is rapidly heated by conduction from steam, radiation from reactor walls, and by direct contact with the trap.

Volatiles released from coal are carried by flowing steam to the reactor outlet and expanded to atmospheric pressure with a residence time of 3 to 5 seconds. A fraction of the product gas stream is conducted to an on-line mass spectrometer for analysis. The only carbon containing gases observed in significant amounts (over 1%) are CO, CO_2, and CH_4. The reaction is terminated by flooding the reactor with helium. Following steam pyrolysis, the residual char is burned with oxygen at 14 atm and the amount of CO_2 produced is used to determine the quantity of carbon remaining in the reactor (the amount of CO produced has been found to be negligible).

This information is used to construct a carbon balance. Total volatile yield is obtained by subtracting carbon determined in residual char from the carbon content of the coal sample charged. The difference between the carbon yields of these gases and the total volatiles yield is ascribed to liquids.

Both pretreated and raw coal are injected into the reactor and pyrolyzed following identical procedures as described above. Pretreatment when desired, is carried out in a preliminary step on the coal charged to the injection tube. An auxiliary heating mantle is placed around the injection tube which is then heated to above the steam condensation point (264°C) while charged with helium. Steam is then admitted to the reactor, and its flow through the coal sample regulated by the vent valve above the injection tube. Temperature during pretreatment is read with a thermocouple spot welded to the outside of the injection tube and controlled by adjustments to the power supplied to the auxiliary heater and the steam flow. Pretreatment is terminated by lowering the temperature while flushing with helium. The sample may then be injected at any time without any intervening exposure to air.

In separate experiments it has been determined that a 7% weight loss occurs by volatilization during pretreatment. This is reported as part of the total volatiles yield. Even though some fraction of volatile material produced during pretreatment is condensable liquid, this has not been included in the liquid yields given below.

Tests were conducted using a batch of Illinois No. 6 coal ground under inert atmosphere to pass 200 mesh and having the following elemental analysis (wt. %) on a moisture free basis: 69.1 C, 5.2 H, 1.2 N, 3.0 organic S, 9.2 organic O, 12.3 mineral matter.* Coal was charged to the reactor with a moisture content of 2.3%.

From 150 to 250 mg. of coal were charged to the reactor in each run. Charges larger than 250 mg. give lower liquid yields, possibly exceeding the ability of the system to rapidly heat injected material.

Further details of equipment and methods are given in Graff, et al, (1983).

Experimental Results

Fig. 2 shows yields obtained from Illinois No. 6 coal over a range of pyrolysis temperatures both with and without pretreatment. In each case pyrolysis was carried out in pure steam at 50 atm. pressure under rapid heating conditions. When the coal is not pretreated, no more than about 23% of its carbon is converted to liquid, the same as has been reported in the literature for pyrolysis in an inert atmosphere at the same pressure (Howard, 1981). Pretreated samples in Fig. 1 were exposed to 50 atm. of steam for 30 minutes at temperatures from 300 to 360°C. By this pretreatment, at a pyrolysis temperature of about 940°C, the liquid yield is more than doubled and the total volatiles yield is increased by about 20%.

While some variation in temperature during pretreatment could not be avoided, it is possible to give approximate limits within which the procedure is effective. Steam was admitted when the saturation temperature had been safely passed, usually at about 300°C. If the sample was not then allowed to reach at least 320°, little, if any, yield improvement resulted. If a temperature much above 360° was reached at any time, the benefits of pretreatment were lost. These limits are likely peculiar to the coal, the pressure, and the exposure time employed and are expected to be different if any of these parameters are changed.

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For commercial processes shorter pretreatment times will be desirable. This possibility has been tested in a few exploratory runs (Table 1). Two runs were made for 15 min. of pretreatment and two for 5 min. of pretreatment. Yields are more sensitive to pretreatment temperature at these shorter times than for the 30 min. pretreatments. In run E113, the sample was pretreated for 15 min. at temperatures mostly around 320°C. Both total volatiles and liquid yields were considerably lower than for 30 min. pretreatments. Yields were brought into agreement with the 30 min. pretreatment in run E114 by keeping the pretreatment temperature mostly in the 330 to 340°C range. A 5 min. pretreatment, mostly at about 340°C, gave low volatiles yield but good liquids yield (E115). When the sample was held at about 350°C for the 5 min. pretreatment, the volatiles yield was raised to the value obtained in 30 min., liquid yield not determined (E117).

The equipment used here is not suitable for studies of pretreatments less than 5 min. in duration. However, results so far suggest that good liquid yields can be maintained with even shorter pretreatments.

A second series of runs were made to test the effect of sample storage between pretreatment and pyrolysis (Table 2). In runs E93, 95 and 98 batch samples of about one gram were pretreated. After cooling in helium, the light agglomerates which had formed were easily broken up and stored in small vials. During handling and storage, no precautions were taken to exclude air. After the time period noted, the sample was reacted in the usual way. All samples show volatiles yields less than that for untreated coal and liquid yields about the same as untreated coal. One sample (E126) was contacted with air for only 2 min. after cooling in helium. Volatiles yield was slightly higher and liquids yield the same as for untreated coal.

It seems possible, however, to store pretreated coal under inert gas. Storage for four hours in helium (Table 2) gave the same volatiles yield as pretreated and promptly injected coal (E120, no liquids yield available). We have no explanation for the anomalously high yield in E118 and have disregarded this run for the present. A sample stored for 18 hours in helium gave higher yields of both volatiles and liquids than promptly injected coal (E127). However, this sample was heated to 226°C and may have received further exposure to steam in the minutes before injection; verification of the results of run E127 will be required.

Six coal samples have been pretreated in helium at 50 atm. pressure. In the temperature range between 315 and 350°C an increase in volatiles yield is observed over that obtained from raw coal. Whether this increase is as much as that obtained from steam is not yet certain; the one available liquid yield is not better than for untreated coal.

Discussion

In general, scant attention has been given to processes occurring in coal below 350°C. In spite of reports to the contrary (*vide infra*), the prevailing opinion seems to be that little of interest occurs below this temperature. For example, Brown and Waters (1966) state that initial softening takes place between 350 and 400°C. Similarly, Neavel (1982) gives 350-450°C as the range in which plastic coals soften and become deformable when heated in an inert atmosphere.

We have observed, however, that our sample of Illinois No. 6 coal looses volatile matter and becomes lightly agglomerated during the pretreatment process even at temperatures as low as 320°C. Consequently, plastic development has at least been initiated. That this has occurred at an unusually low temperature may be a result, in part, of the elevated pressure which retards loss of volatiles. Some chemical, or physical activity of steam may also play a role.

The literature does contain reports of coal activity below 350°C (Kirov and Stephens, 1967). Berkowitz (1957) reported exotherms commencing near 200°C which reached a maximum between 260 and 280°C and the appearance of slight exotherms around 320 to 340°C in the differential thermal analysis of five bituminous and sub-bituminous coals. Some very pronounced endotherms appear in differential scanning calorimetry curves at about 300°C for various coals (particularly for an HVB coal from Illinois) published by Mahajan, et al. (1976).

Thermally induced alterations to the organic structure of coal at low temperature were demonstrated by Chakrabartty and Berkowitz (1977) using sodium hypochlorite oxidation. Heating of Kentucky hvb coal samples for 2 hrs. at temperatures as low as 150°C produced observable changes in carboxylic acid yields from which it was concluded that isomerization was already beginning.

Squires, et al. (1983) found that heating of Illinois No. 6 coal in vacuum caused a reduction in its pyridine solubility beginning at 200°C. A parallel effect was observed when samples heated in flowing methanol were subsequently extracted with pyridine.

These literature references suggest that coal is labile at the temperatures used in the pretreatment process. The limited volatilization and agglomeration observed in the process may result in part from bond rupture. Elevated pressure acts to retard volatiles loss, particularly of heavier species, increasing mobility. This may improve the accessibility of internal donatable hydrogen to free radicals formed by thermal rupture (following the discussion of Neavel, 1982) inhibiting repolymerization and resulting in a partially depolymerized material. All of these effects could occur during heating in an inert atmosphere under pressure, and we have observed increased volatiles yields resulting from such treatment. In steam, these effects may be enhanced or supplemented by other processes discussed below.

Pretreated coal has been found to be very sensitive to exposure to air. Oxidation of coal is known to reduce its plastic properties and lower liquefaction yields, an effect attributed to the formation of cross-links. A similar effect may be operative when pretreated coal is exposed to air. It's extreme sensitivity suggests that the material is somehow unstable and quite susceptible to cross-linking by oxygen.

Our observations indicate that steam is considerably more effective in pretreatment than an inert atmosphere. An explanation may be found in the work of Ross et al.(1982) who reacted anisole at 400°C in 184 atm. (estimated) of D_2O. At this temperature the calculated half-life of the ether linkage for thermal rupture is 29 hours. Yet, in deuterated steam the observed conversion is about 30% in 20 minutes. To the extent that anisole is a model for ether-aryl linkages in coal, this implies that steam has the ability to "depolymerize" coal by cleaving these thermally stable linkages. Ross (1983) has further found that steam, under the same conditions, removes 40% of the coal's oxygen. Although his work was carried out at higher temperatures and pressures, it nevertheless suggests that steam has important chemical activity in the pretreatment process.

Another effect at work in pretreatment is the mutual solubility of water and hydrocarbons. Although mutual solubility is quite low at ordinary conditions, they become miscible in all proportions at high temerpature and pressure (Schneider, 1970). In the naphthalene-water system, for example, the critical solution temperature is as low as 310°C and 100 atm. Even though miscibility may not be complete at pretreatment conditions (the pressure is lower) wide regions of solubility are likely. This would have the following consequences: to the extent that water dissolves in the plastic or molten coal, its mobility is increased thus improving transfer of internal donatable hydrogen. It also places water into intimate contact with coal for chemical reaction, and makes ionic reactions possible. To the extent that large aromatic hydrocarbon fragments dissolve in a water phase, the rate of their repolymerization is reduced by dilution.

Conclusions

From the experimental results and discussion above, we conclude that important changes in the structure of coal occur at temperatures below 350°C. Although a number of potential explanations may be suggested, it seems likely that coal is partially depolymerized during pretreatment, resulting in higher yields of volatiles in a subsequent pyrolysis. The effect is not solely thermal; the presence of water significantly improves product yields.

An evaluation of liquid quality is needed to evaluate the full potential of steam pretreatment. However, provided the liquids are of acceptable quality, the beneficial effects of pretreatment are such as to increase liquid yields in pyrolysis to levels of commercial importance.

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Table 1. Steam Pyrolysis of Pretreated Coal. Prompt Injection

Run No.	Pretreatment Time Min.	Pretreatment Temp. Range (C)	Wt. Loss%	Pyrolysis Temp. (C)	Carbon Conversion (%) CH_4	CO	CO_2	Liquids	Total Volatiles
E113	15	301-348	(7)	933	3.9	12.7	12.2	35.9	71.7
E114	15	260-353	(7)	923	2.4	3.7	10.1	54.9	78.1
E115	5	286-340	(7)	918	1.8	1.6	5.6	49.4	65.4
E117	5	313-370		946					82.5

Table 2. Effect of Storage in Air and Helium on Steam Pyrolysis Yields of Pretreated Illinois No. 6 Coal

Run No.	Pretreatment Time (Min)	Pretreatment Temp. Range (C)	Wt. Loss%	Storage Time	Storage Medium	Pyrolysis Temp. (C)	Carbon Conversion (%) CH_4	CO	CO_2	Liquids	Total Volatiles
E93	30	265-339	7.8	12 days	Air	920	2.9	5.4	13.7	25.7	55.5
E95	30	289-335	(8)	4 days	Air	914	2.0	5.4	20.7	14.8	53.4
E98	30	289-335		25 days	Air	924					44.5
E118	15	274-358		4 hrs.	He	914					94.0
E120	15	288-377		4 hrs.	He	913					74.9
E126	15	311-358	(7)	2 min.	Air	920	3.9	7.4	20.2	25.5	64.0
E127	15	299-362	(7)	18 hrs.	He	912	3.4	2.1	12.7	61.3	86.5

( ) estimated from direct measurements on other samples.

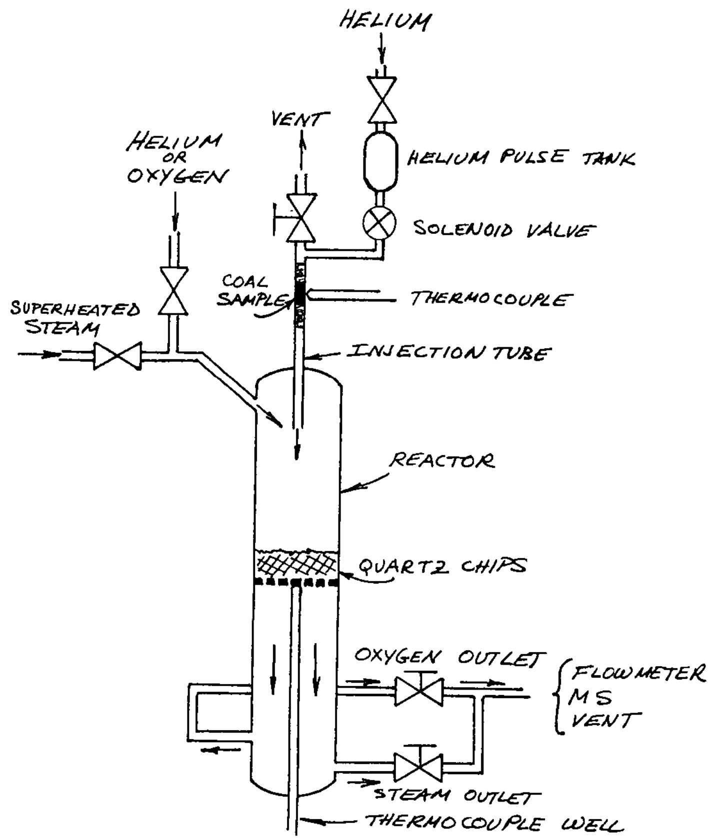

Fig. 1. Coal Injection Reactor for Pretreatment and Flash Pyrolysis

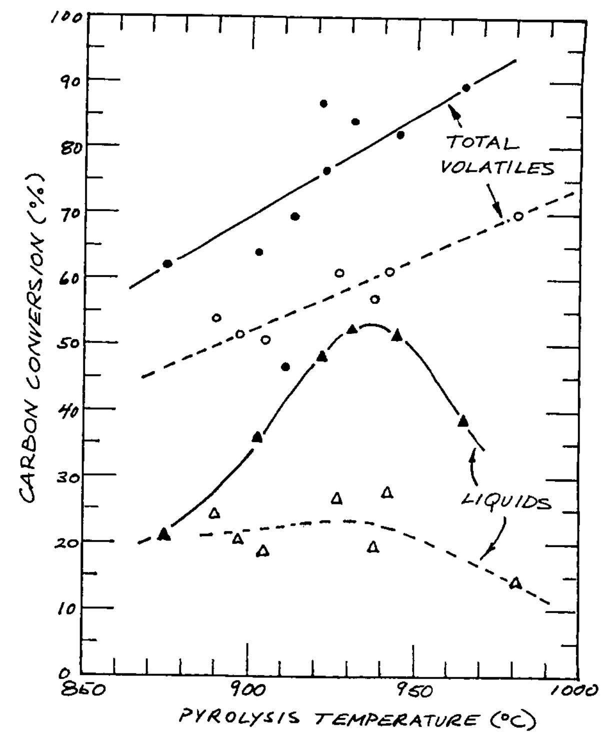

Fig. 2. Comparison of Steam Pyrolysis Yields obtained from As-received (open points) and Pretreated (closed points) Illinois No. 6 Coal at 50 Atm.